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16. ABSTRACT The STEM-II model was applied to a case study of the acid deposition upwind and downwind of Philadelphia Pennsylvania. The model has the Atkinson-Lloyd kinetics mechanism for gas phase chemistry and an aqueous phase mechanism for 22 species. The model results indicate that the major trends in the data are correctly simulated. Time histories at particular grid locations are consistent with the known meteorological conditions.					
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AN EVALUATION OF THE CHEMICAL AND PHYSICAL PROCESSES AFFECTING SULFATE AND NITRATE WET DEPOSITION

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INTRODUCTION

The assessment of the effect of a reduction in primary emissions of SO_x , NO_x , and hydrocarbons on the pH of rain, on the ambient sulfate and nitrate levels, and on the total deposition amounts of sulfates and nitrates is currently one of the most important environmental challenges. However, the relationships between the emissions and the resultant distribution of acids and acidic precursors are difficult to determine because of the number and nature of the processes that occur. For example, the convective and diffusive processes, the in-cloud meteorology and chemistry, the homogeneous gas phase chemistry, and the deposition processes all influence the source receptor relationships.

In order to better understand these complex relationships a detailed combined transport/chemistry/removal model (referred to as STEM-II) has been developed by Carmichael et al., 1986. In this paper the wet deposition of sulfate and nitrates are investigated using the STEM-II model. The discussion includes an evaluation of the various chemical and physical processes contributing to sulfate and nitrate concentrations in hydrometeors and the diagnostic analysis of the primary processes in a mesoscale deposition event that occurred in the Philadelphia area on May 2nd 1985.

DESCRIPTION OF STEM-II MODEL

The STEM-II model (Carmichael et al., 1986) is an Eulerian combined transport/chemistry/removal model which treats chemical species in the gas, cloud, rain and snow phases. Thirty-nine species are advected, while twenty-one species are short-lived and are modeled using pseudo-steady state methods. The advected species satisfy the following equations

Gas Phase:

$$\frac{\partial C_i}{\partial t} + \frac{\partial (U_j C_i)}{\partial x_j} = \frac{\partial}{\partial x_j} [K_{jj} \frac{\partial C_i}{\partial x_j}] + R_i + S_i + G_i \quad i=1, \dots, 39 \quad (1)$$

Cloud, Rain and Snow Phases:

$$\frac{\partial (S_m C_{im})}{\partial t} + \frac{\partial}{\partial x_j} (U_j - v_{sm}) S_m C_{im} - \frac{\partial}{\partial x_j} (K_{jjm} C_{im} \frac{\partial S_m}{\partial x_j} + R)_{im} + G_{im} \quad (2)$$

$i=1, \dots, 39$ $m = 1$ for cloud ($v_{sm} = 0$)
 $m = 2$ for rain
 $m = 3$ for snow

where C_i 's denote the concentrations,
 U_j 's are velocity components,
 S 's are the liquid water contents,
 v_s 's are the settling velocities of the hydrometeors,
 K_{jj} 's are the eddy diffusivities, and
 R_i , G_i and S_i are the rates of chemical reaction,
 mass transfer, and emissions, respectively.

The STEM-II model is structured to treat in detail wet removal processes. The physical processes of nucleation, accretion, autoconversion, and riming are included in the model analysis. In this model, the in-cloud scavenging of sulfate aerosol is presumed to occur totally by nucleation. Both cloud and aerosol size distributions are assumed to be monodispersed. Once the cloud forms, the number of sulfate aerosols activated and dissolved to form aqueous sulfate is assumed to be the same as the number concentration of cloud droplets. Rain drops are also assumed to be monodispersed. Secondary sulfate is treated in the same way as primary sulfate and is allowed to be reinjected into the gas phase as hydrometeors evaporate.

The cloud parameters are calculated by the ASM cloud scavenging model (Hales, 1984). The ASM model treats the cloud microphysics and calculates the cloud and precipitation distributions, and interconversion rates. ASM calculates a self consistent and realistic meteorological data set of the simulated storm. The precipitation-formation processes are treated in a parameterized fashion. The parameterizations of rain-formation are adapted from Berry and Reinhardt (1974), Scott (1982), Kessler (1969), and Lin et al., (1983). The snow-formation is parameterized based on schemes similar to that developed by Lin et al., (1983) and Scott (1982). The scheme lumps water into four categories: water vapor, cloud water, rain and snow. The cloud related parameters calculated in ASM are transferred to the STEM-II model where the transport/chemistry/removal of pollutants is calculated.

For the gas phase, the new reaction mechanism of Atkinson and Lloyd (1982) which includes 81 reactions and 60 chemical species, is used. Of these species, 39 long-lived species are advected while the remaining 21 short-lived species such as free radicals are modeled using Pseudo Steady State Approximation.

In addition, for the liquid phase, 16 dissociation expressions, 33 chemical reactions and 22 ionic species based on the work of Chameides et al., (1984) are included in the STEM-II code. Detailed solution equilibria and chemical kinetics are solved using a modified semi-implicit method while satisfying the electrical-neutrality constraint. Also, the mass transfer associated with absorption into, and desorption from droplets is included.

The effect of clouds on the solar flux values is also included in this analysis. The following empirical correlation relating photon flux to cloud cover (Kaiser and Hill, 1976) is employed.

$$F = F_c(1 - AC^{1.75})$$

(3)

where F_c is the photon flux for clear sky, C is the cloud cover fraction, and A is a constant dependent on cloud type.

The numerical integration of the model equations makes use of the concept of fractional time steps and one-dimensional finite elements; referred to as the Locally One-Dimensional Finite Element Method (LOD-FEM). The transport equations are solved using a modified Galerkin FEM with asymmetric weighting functions and the Crank-Nicolson method for time. The chemistry equations are solved using a modification of the semi-implicit Eulerian method. Details of the numerics used in the model are found in Carmichael et al. (1986).

RESULTS AND DISCUSSION

The STEM-II model is being used to analyze field data collected in the U.S.E.P.A. Mesoscale Acid Deposition Study. The purpose of the study is to assess the importance of local emissions on the wet deposition loadings at receptors located within 200-300 km of urban centers. Discussions here will focus on the analysis of the May 2nd field study conducted in the Philadelphia area.

The modeling domain used for this analysis is shown in Figure 1. Two different grid systems are being used: a coarse grid with horizontal grid spacings of ~ 56 km; and a fine grid with horizontal spacings of 20 km. The vertical domain is the same in each system with 14 vertical grids non-uniformly spaced between the surface and a height of 6 km. The wind, temperature, and surface precipitation fields predicted by the dynamic meteorological model MASS (cf, Kaplan et al., 1982) were used as inputs to the STEM-II model. The predicted precipitation fields were used as inputs to the ASM cloud model to generate the microphysical parameters for the wet removal calculations.

The emissions fields for the simulations were based on Version 5.2 of the U.S.E.P.A. inventory which includes SO_x , NO_x , and speciated hydrocarbons. Point sources of SO_2 and NO_x in the region are shown in Figure 2. As shown, the Pennsylvania side of the domain (the west half of the region) has many sources, while the New Jersey side (the east half of the region) is a relatively low source region.

The May 2nd event was an example of a slow moving frontal system which produced very heavy precipitation in the study area. The flow field in the modeling region at 14:00 LT (local time) was generally from the east and gradually shifted from the northeast at 22:00 LT. The wind speeds were high throughout the period with horizontal winds of 15 m/s. The precipitation came from the south and reached Philadelphia at 15:50 LT.

The measured wet deposition loadings of nitrate and sulfate are shown in Figure 3. The general features show that for both species the loadings were higher on the Pennsylvania side. Furthermore, the nitrate loadings were slightly higher than those for sulfate on the New Jersey side.

Coarse grid model predictions are presented in Figure 4. The results are for an 18 hr period corresponding to 14:00 May 2nd to 8:00 May 3rd, 1985. The model was initialized by starting with remote

conditions and then seasoning under no-flow conditions with real emissions for a period of 2-3 days. The chemical composition of the air masses transported into the model region (through the eastern and northern boundaries) was estimated by performing 1-dimensional model calculations reflecting the air mass histories. For example, the air entering through the eastern boundary has relatively low concentrations reflecting that it originated from the south and traveled along a wet trajectory, whereas the air mass entering the northern boundary has high concentrations of pollutants reflecting the high sources regions upwind in New York.

Predicted total 18 hr wet deposition loadings of selected species are presented in Figure 4. The sulfate and nitrate loadings show similar general features. The deposition values are much higher in the western part of the region and the nitrate values are somewhat higher than the sulfate levels. The regions of deposition loadings greater than $1000 \mu \text{mole m}^{-2}$ are found downwind of the major sources (recall the flow is originally from the east and later from the northeast).

The deposition loadings of bisulfite and H_2O_2 are also presented. The bisulfite loadings are from 3-5 times lower than those for sulfate. The general pattern for bisulfite and H_2O_2 appear to be anticorrelated with high bisulfite and low H_2O_2 loadings occurring in the north and west regions and low bisulfite and high H_2O_2 loadings in the south and east regions. The pattern of the H_2O_2 loadings is quite similar to that for the total predicted precipitation loading.

The predicted deposition loadings are in good agreement with the measured values (see Figure 3). The average predicted values of sulfate and nitrate in the areas of measurements on the Pennsylvania and the New Jersey side are 417 and 305 for sulfate, and 623 and 374 $\mu\text{H/m}^2$ for nitrate, respectively.

Further details of the deposition at the New Jersey measurement sites and the Pennsylvania sites can be seen by examining the deposition as a function of time at grid points (2,4) and (4,2) (see Figure 1). The time profiles of surface gas phase and rain phase concentrations of selected species are presented for comparison in Figure 5. The New Jersey site is an area of low NO_x and SO_x sources and for the meteorological conditions on May 2nd the wind direction is from the east; thus, relatively clean air is passing to this site through the eastern boundary. Precipitation occurs at this grid point for the first 16 hours of the event. The rain phase concentrations at this grid point show that the soluble pollutants are removed rapidly by the initial rain and that the bulk of the deposition loading occurs in the first hour of the rain event. The liquid phase concentration of H_2O_2 builds up beginning 1:00 LT on May 3rd. This corresponds to the time that the wind shifts to a northeasterly flow transporting polluted air mass reaching this site.

The Pennsylvania site (grid point (2,4)) is located in a region with high SO_x and NO_x emissions. The site is also downwind of major sources throughout the meteorological conditions of May 2nd 1985. Precipitation began at this site at 17:00 LT May 2nd and continued until 4:00 LT on May 3rd. The time profiles of gas and liquid phase concentrations at this site are also presented in Figure 5. The time profiles are quite different than those at the New Jersey site. The liquid phase concentrations of most species reach maximum values at 19:00 LT. The nitrate concentration maximum is $\sim 200 \mu\text{M}$ while that of sulfate is $\sim 100 \mu\text{M}$. The liquid phase concentration profiles of H_2O_2 and bisulfite show opposite trends. The H_2O_2 is high initially

decreases as time progresses. This indicates that at early times H_2O_2 is present in excess of bisulfite, and the bisulfite is consumed by the reaction with H_2O_2 to produce sulfate. At later times the H_2O_2 is depleted from the system and the bisulfite concentration increases. The gas phase profiles (not shown) indicate that gaseous H_2O_2 is depleted from the area by 22:00, whereas gaseous SO_2 is maintained by local emissions.

The mass balance inventories for the 18 hour simulation are presented for HNO_3 , sulfate and SO_2 in Figure 6. These results useful insights into the relative importance of various processes. The SO_2 inventory shows that local emissions during the 18 hour period is equivalent to about 1/3 of the mass of SO_2 initially present. (Furthermore, the net advection into the region is equivalent to the amount emitted). The wet deposition and dry deposition are of equal importance and together are equivalent in magnitude to the emissions. The wet removal processes consists of wet deposition of S(IV) at the surface and the conversion of S(IV) to sulfate in cloud and rain water. As indicated the importance of liquid phase consumption of S(IV) is much more important than the gas phase destruction reactions of SO_2 . The predominant liquid phase reaction for this simulation is the reaction of S(IV) with H_2O_2 to produce sulfate. The inventory for sulfate reveals that the contribution of primary emissions is very small, that wet deposition is much more important than the dry deposition process for this event, and that sulfate production by liquid phase processes greatly exceeds that in the gas phase. The nitrate inventory is similar to that for sulfate except that there were no liquid phase production or consumption reactions involving nitrate included in the analysis.

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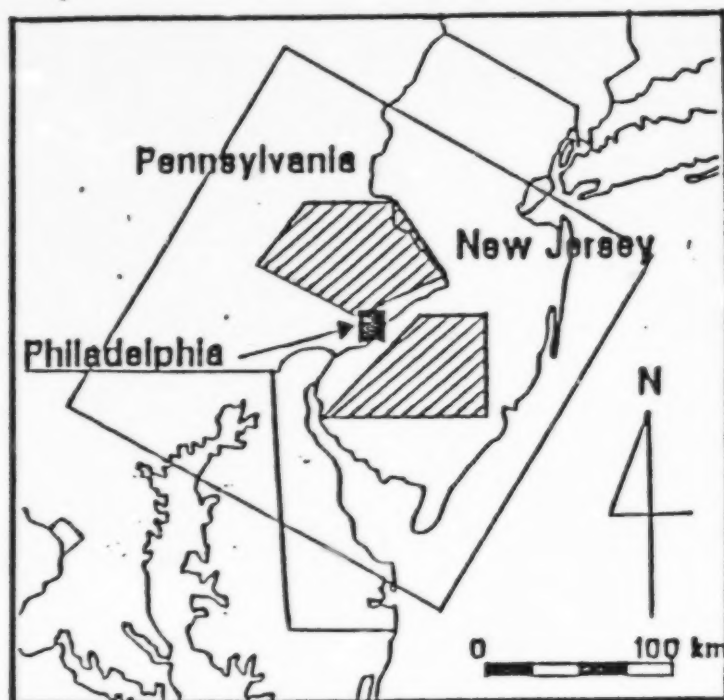
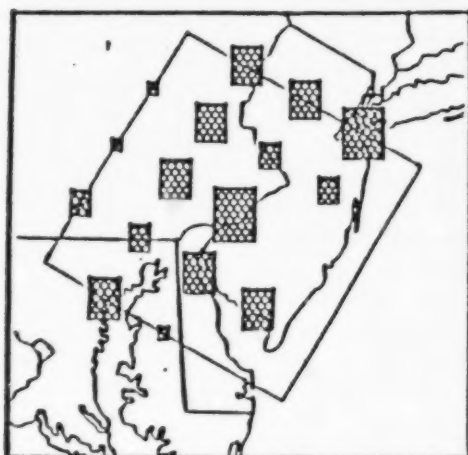
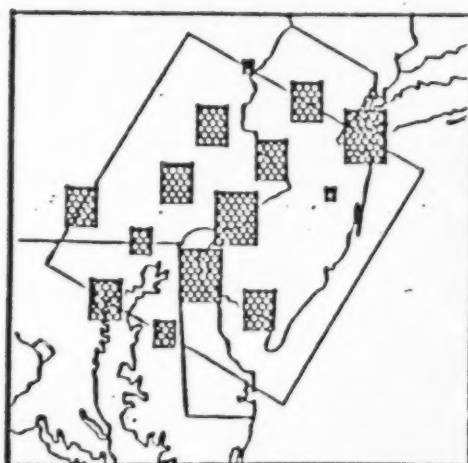
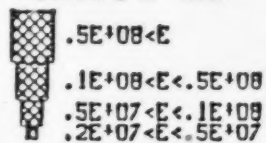


Fig. 1. Philadelphia mesoscale acid deposition study domain. The shaded regions denote the areas where the monitoring stations were deployed. The large slanted square represents the modeling region.



(a)

molecule. $m^{-2} sec^{-1}$



(b)

molecule. $m^{-2} sec^{-1}$

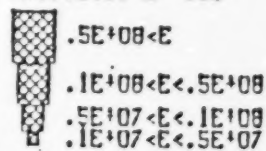


Fig. 2. The point source emissions of (a) NO and (b) SO₂ at the surface.

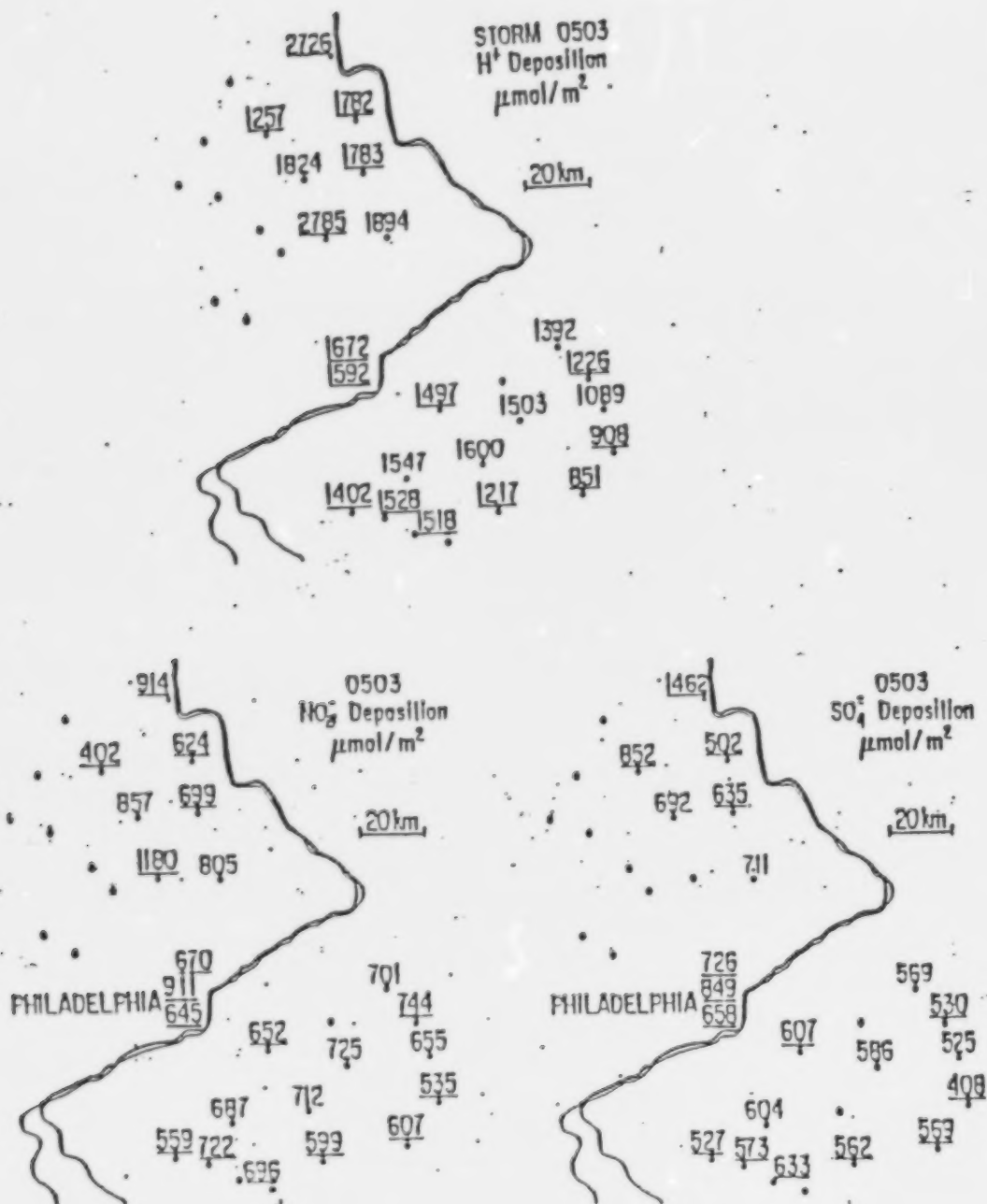


Fig. 3. Measured total deposition of (a) H^+ , (b) HNO_3 , and (c) SO_4^{2-} .

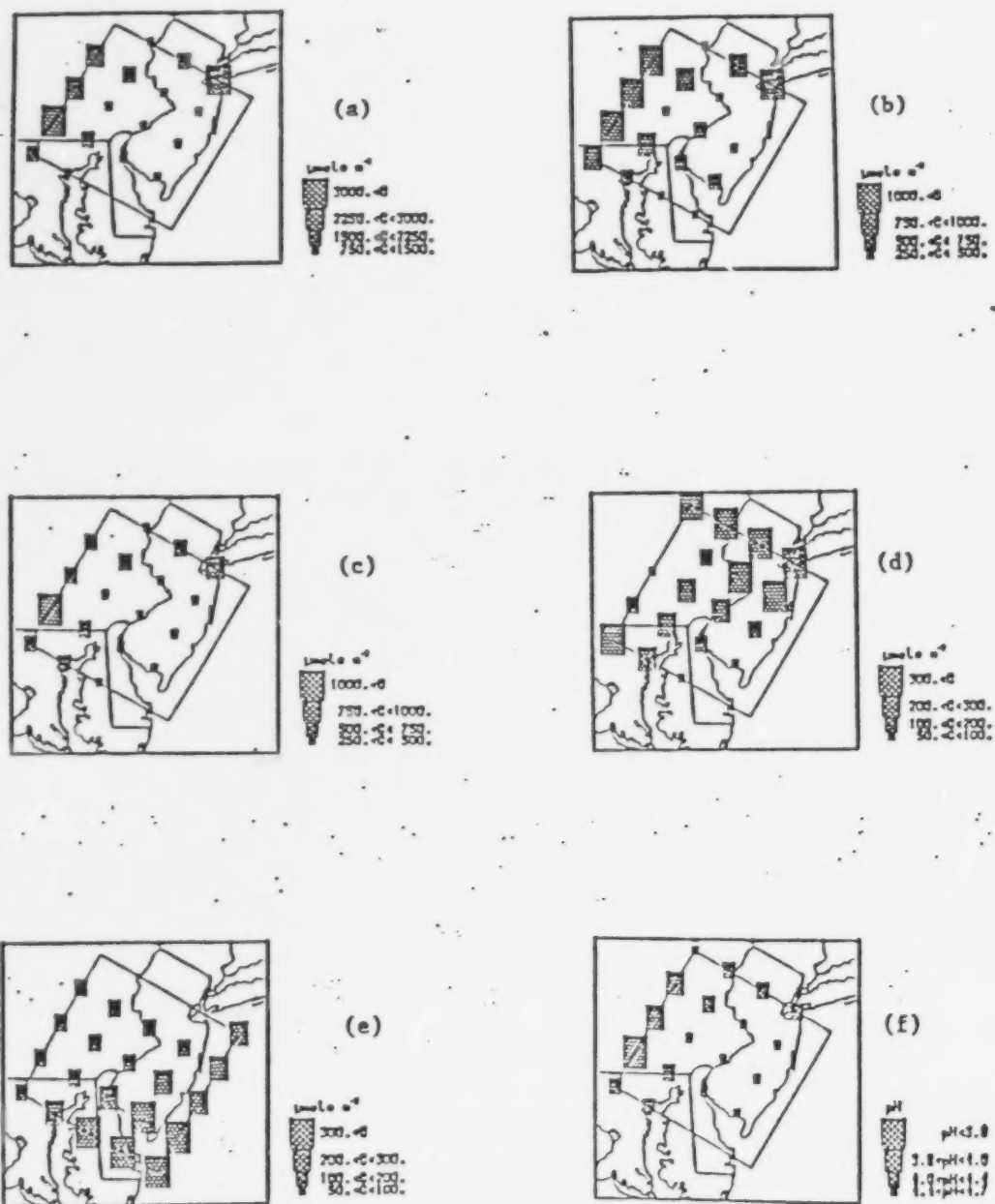


Fig. 4. Predicted total deposition of (a) H^+ , (b) HNO_3 , (c) SO_4^{2-} , (d) bisulfite, (e) H_2O_2 , and (f) 18 hr averaged pH of rain during the storm.

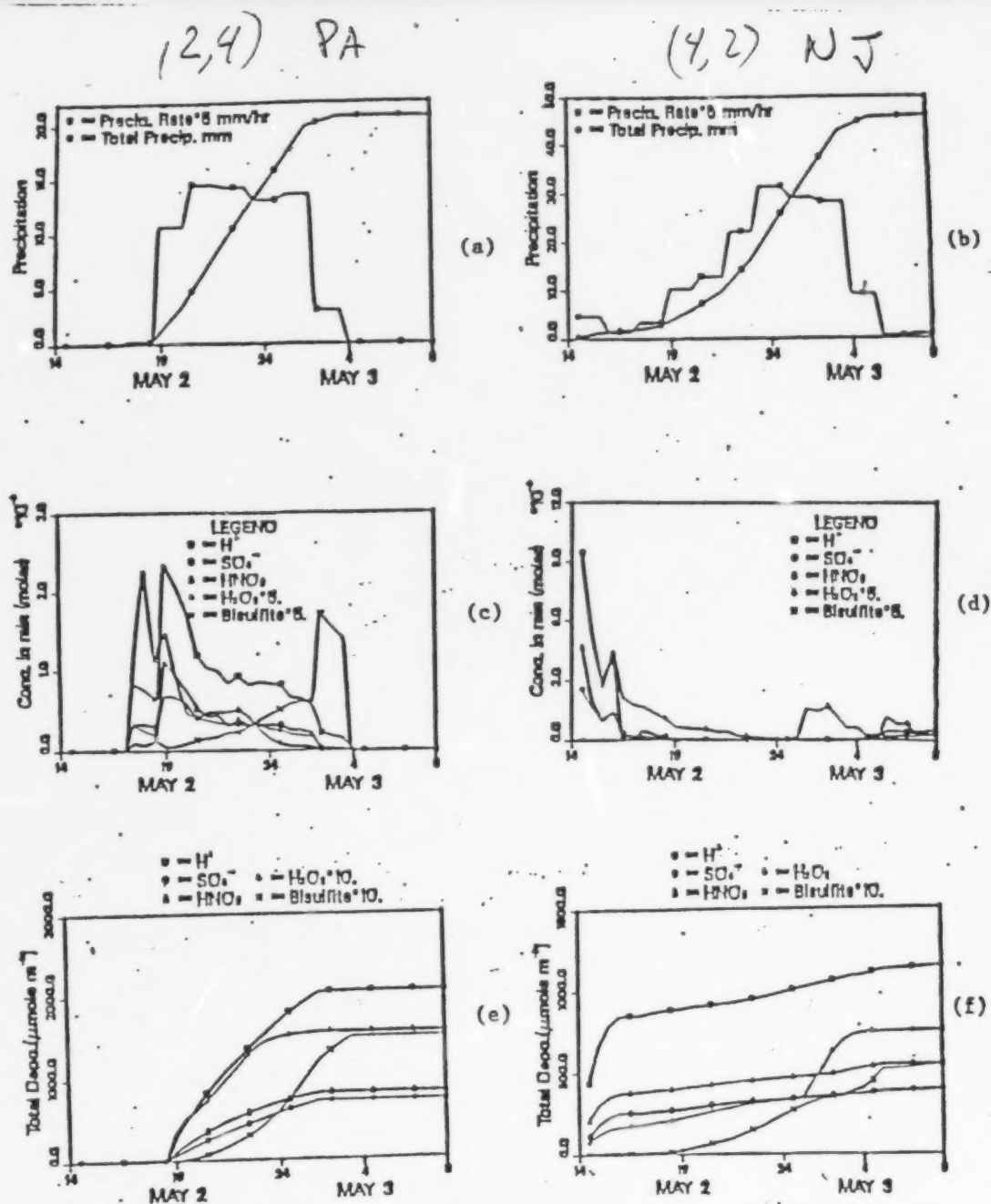


Fig. 5. (a) Precipitation field at grid (2,4), (b) precipitation field at grid (4,2), (c) instantaneous deposition at grid (2,4), (d) instantaneous deposition at grid (4,2), (e) cumulative deposition at grid (2,4), and (f) cumulative deposition at grid (4,2).

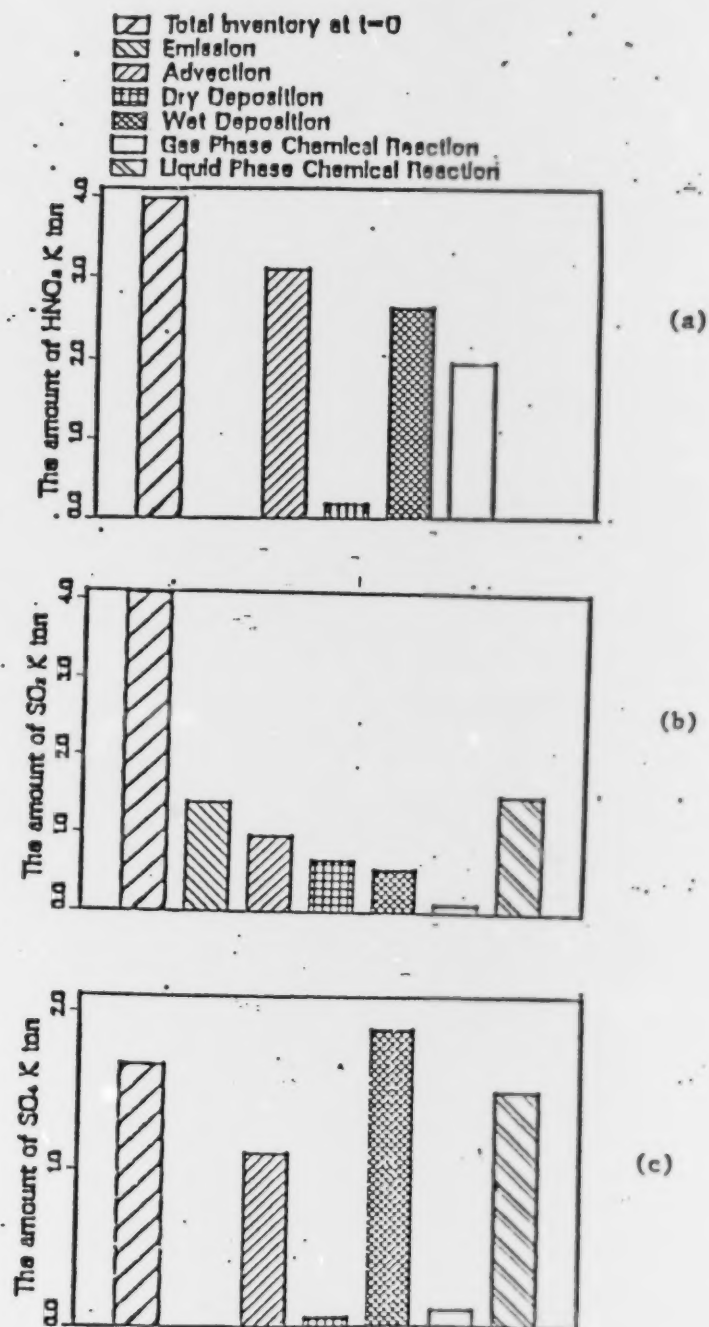


Fig. 6. Inventories of (a) HNO_3 , (b) SO_2 , and (c) SO_4 .